

Size and Composition Distribution of Atmospheric Particles in Southern California

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Continuous measurements of single particle size and chemical composition in the atmosphere are made using aerosol time-of-flight mass spectrometers (ATOFMS) operated alongside more conventional reference air sampling instruments at a network of three urban air monitoring sites in southern California. Electrical aerosol analyzers and optical particle counters are employed to acquire continuous particle size distribution data, and inertial impactor and bulk filter samples with 4-h resolution are taken for determination of particle size and chemical composition. Filter and impactor samples also are taken upwind of the air basin at Santa Catalina Island in order to characterize background air quality. The airborne particle size and composition distribution as measured by the cascade impactors at inland sites differ from that over the ocean principally due to depletion of sea salt particles accompanied by the addition of fine carbon-containing particles and secondary aerosol nitrate. Data from the ATOFMS systems create a continuous time series of sodium-, ammonium-, nitrate-, and carbon-containing particle counts that provide a high-resolution view of differences in particle composition as a function of location in the air basin. Results show that the characteristic peak in the Los Angeles area aerosol mass distribution in the 0.2–0.3- μm size range observed during the 1987 SCAQS experiments has been reduced, consistent with reductions in diesel soot and elemental carbon emissions since that time.

Introduction

The size and composition of airborne particles evolve over time in the atmosphere as the direct primary emissions of new solid and liquid particles from emissions sources in a city are mixed with regional background aerosol present due to long-distance transport. Emitted particles and background aerosol also are transformed by interaction with gaseous air pollutants. For example, SO_2 oxidation leads to secondary sulfate accumulation on the preexisting particles (1). Organic

vapors can react to produce low vapor pressure products that subsequently become distributed onto the aerosol (2). Nitric acid vapor reacts in the atmosphere with ammonia to produce ammonium nitrate aerosol (3–6), and nitric acid also can react with sea salt particles to produce sodium nitrate particles (7).

The size and chemical composition distribution of the airborne particle mixture within an air basin depends on how these secondary reaction products are distributed across the underlying primary particle size distribution. To control the effects of exposure to airborne particles, it is necessary to know how emissions control decisions will affect the concentration, size, and composition of the particles. Particles of different sizes have different effects on visibility (8–10) and differ greatly in terms of their locations of deposition in the lung (11).

Interaction between the gas and particle phases occurs at the single particle level. Individual particle size and hygroscopicity, and thus chemical composition, determine whether a particle will activate when fog forms, thereby facilitating sulfate formation by liquid-phase chemical reactions. Whether or not organic vapors can partition into a particle likewise depends on the organic chemical constituents of the single particle. Knowledge of single particle composition is needed to study these processes, but in the past with a few exceptions (e.g., ref 12), the available information on the chemical components of particles has existed largely in the form of bulk chemical composition data taken from filter samples in which a large number of particles are mixed together during collection and subsequent chemical analysis.

Recent air quality modeling approaches are capable of describing gas/particle interactions at the single particle level in a complex urban atmosphere (13). In another recent development, new aerosol time-of-flight mass spectrometers (ATOFMS) can be used to measure the size and mass spectrum of single particles (12, 14–23). The purpose of this paper is to describe the design and execution of an experiment that deploys these ATOFMS systems alongside more conventional reference method instruments to observe and record single particle characteristics that can later be compared to air quality models that predict particle size and composition at the single particle level.

Three air monitoring stations were established in mid-September, 1996, and operated through early October, 1996, along a seasonally typical air parcel pathway crossing the Los Angeles Basin. A fourth temporary station was established at an offshore island upwind of these three sampling sites to measure background particle concentration, chemical composition, and size distribution. Data on single particle size and chemical characteristics were collected continuously at each urban air monitoring station by aerosol time-of-flight mass spectrometers (12, 14). Particle size distributions also were measured continuously by electrical aerosol analyzers and laser optical particle counters. On certain days size-segregated, fine, and total suspended particulate matter samples of 4-h duration were collected for comprehensive chemical analysis at each site, using a low-volume filter-based sampling system and a pair of microorifice impactors (MOIs) at each site.

These measurements serve many purposes. First they provide a description of particulate matter characteristics as a function of particle size, chemical composition, and time in the Los Angeles Basin, which is the subject of the present paper. The data later will be used to study the evolution of individual air parcels in a Lagrangian framework as they pass

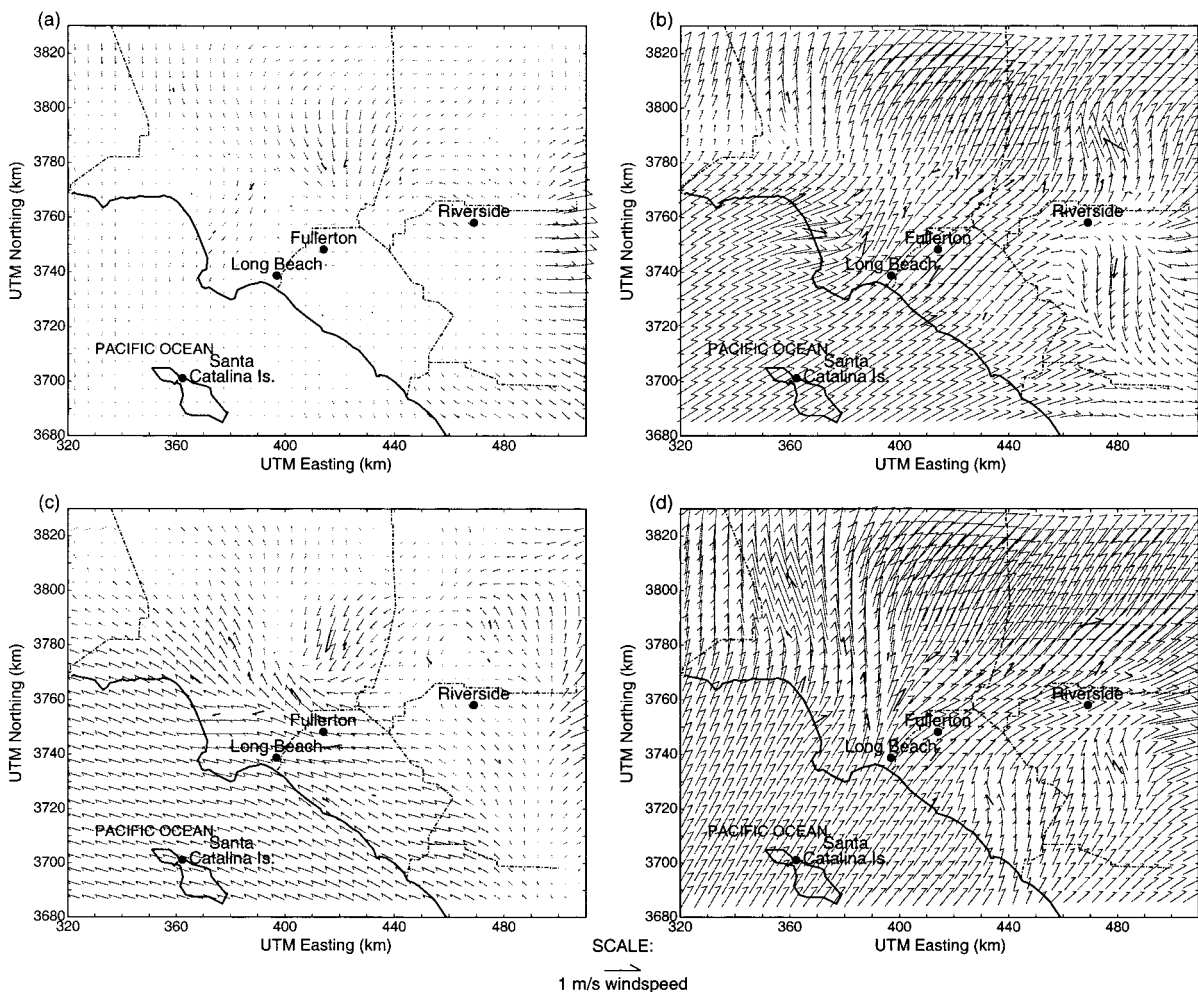


FIGURE 1. Surface windfields over the study area at (a) 0600 PDT on September 23, 1996; (b) 1300 PDT on September 23, 1996; (c) 0600 PDT on October 1, 1996; (d) 1300 PDT on October 1, 1996. Sampling site locations used in these experiments are indicated on the map.

over successive air monitoring sites. In future work, the number distribution, mass distribution, and size-resolved chemical composition data taken by the conventional reference air sampling instruments will be used to calibrate the counting efficiencies and chemical sensitivities of the ATOFMS instruments under field sampling conditions in order to render the ATOFMS data into a quantitative description of particle size and composition. Ultimately, these data are intended for use as a model evaluation data set for air quality models that predict the size distribution and chemical composition of individual particles in the atmosphere (7, 13).

Related Studies

The South Coast Air Basin (SoCAB) surrounding Los Angeles, CA, has been the focus of extensive studies of urban photochemical smog formation. Experiments employing multiple sampling sites to simultaneously examine atmospheric aerosols at locations across the basin have been conducted since the early 1970s. The California Aerosol Characterization Experiment (ACHEX) (24) yielded data on particle size distributions and chemical composition measurements at up to five sites in the SoCAB between September 1972 and October 1973. Lundgren impactor samples and bulk aerosol filter samples were analyzed by neutron activation analysis (NAA), X-ray fluorescence analysis (XRF), X-ray photoelectron spectroscopy for chemical analysis (ESCA), and various chemical methods to determine noncarbonate carbon, sulfate, nitrate, and trace element concentrations.

Electrical aerosol analyzers (EAAs) and optical particle counters (OPCs) provided detailed information on particle size distributions.

In 1982, ionic aerosol species and gas-phase HNO_3 , NH_3 , O_3 , NO , and NO_x were simultaneously measured with 2-h time resolution over 48 h at 10 SoCAB sites to provide a database from which to evaluate the predictions of both Lagrangian trajectory and Eulerian grid-based air quality models for aerosol nitrate formation (6, 25–27). Analysis of these data showed that inorganic nitrate was distributed between the gas and particle phases in approximate agreement with predictions for the thermodynamic equilibrium between the gas and particle phases (28) and that particulate nitrate formation could be predicted based on NO_x , NH_3 , and organic vapor emissions from local air pollution sources (6, 26, 27).

In the summer and fall of 1987, the Southern California Air Quality Study (SCAQS) was conducted with the objectives of observing particle characteristics and providing data for the evaluation of air quality models for the formation and transport of photochemical oxidants and particulate matter. Collection of particulate matter filter samples having 4–7-h time resolution occurred at nine sites throughout the SoCAB. Aerosol samples were analyzed for carbon, inorganic ions, and elemental composition. Concurrent measurements of gas-phase HNO_3 , NH_3 , SO_2 , O_3 , NO , NO_x , and CO were made along with detailed speciation of volatile organic compounds (29–33). At Claremont, CA, and occasionally elsewhere, measurements of particle size distributions were made with

electronic size distribution monitors, and cascade impactors were used to collect data on particle chemical composition as a function of particle size (30, 31, 33). The extensive database gathered from the SCAQS experiments has been used to evaluate the predictions of a variety of models for secondary aerosol formation, transport, and deposition in the Los Angeles area (2, 13, 34–41) as well as models for light scattering and visibility reduction in the atmosphere (10, 42). The SCAQS experiments did not include measurements of individual semivolatile vapor-phase and particle-phase organic compounds. Data on semivolatile vapor-phase organic compounds are necessary in order to study secondary organic aerosol formation and gas/particle partitioning. Therefore during the summer of 1993, simultaneous short-term time series measurements of particle-phase, gas-phase, and semivolatile organic compounds were made at four urban air monitoring sites and at an offshore island in the Los Angeles area (43–46). Inorganic ions and organic and elemental carbon components of the aerosol were measured as well as gas-phase HNO_3 , HCl , NH_3 , SO_2 , O_3 , NO , NO_2 , and CO concentrations.

The field study described in the present paper differs from previous efforts because it provides the first field experiment in which multiple air monitoring sites equipped with ATOFMS systems have been used to characterize an airshed based on real-time single particle-level size and chemical composition data. The purpose of the present paper is to describe the basic experiment, to present the data on bulk aerosol properties, and to introduce examples of the raw data on single particle composition collected by the ATOFMS systems. The siting of the air monitoring stations is designed to lie along typical air parcel trajectories, and in later analyses single air masses will be studied as they pass over several sites successively, thereby providing unique insights into chemical processes and transformations. Eventually, the data can be used to evaluate the predictions of an existing atmospheric aerosol processes model that predicts both the size and the composition distribution of the aerosol as well as particle-to-particle differences for particles of the same size by separately tracking the individual primary particles emitted from different sources as they become coated by or integrated with secondary aerosol conversion products over time (13).

Experimental Methods

Sampling of size-segregated, fine, and total suspended ambient particles for subsequent chemical analysis and measurement of airborne particle size distributions were conducted over the course of two weeks in late September and early October 1996. Instruments were stationed at three sites in the urban Los Angeles area: Long Beach, Fullerton, and Riverside, CA (see Figure 1). In addition, the upwind background aerosol size distribution and chemical composition was characterized at Santa Catalina Island.

An electrical aerosol analyzer was operated daily at each of the three urban sampling sites; laser optical particle counters were placed at Long Beach and Riverside. In addition to these conventional sampling methods, an ATOFMS was operated continuously at each of the three urban sites. This set of instruments was used to obtain continuous measurements of particle number distribution and single particle chemical composition.

On the basis of weather predictions indicating probable inland air transport, 4 days (September 23 and 24 and October 1 and 2, 1996) were chosen for more extensive sampling. Intensive experiments were conducted over pairs of consecutive days to accommodate the previously observed travel time of air parcels across the basin (6). On these 4 days, the low-volume filter samplers, impactors, and VOC canisters at each site were used for one 4-h period each day (the intensive operating period, or IOP). Two additional days (September

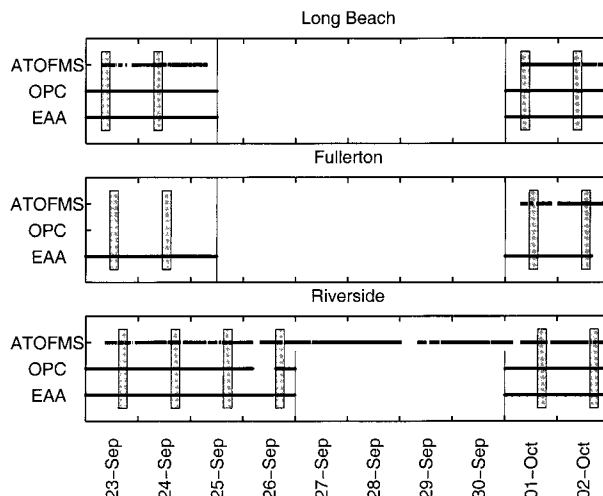


FIGURE 2. Times of operation (in PDT) of ATOFMSs, OPCs, EAAs, and other instruments at each site during the study. Shaded boxes indicate the intensive operating periods; total and fine particle filter samples, size-segregated impactor samples, and VOC canister samples were taken only during these 4-h periods of intensive operation.

25 and 26, 1996) were chosen for intensive sampling at Riverside only because conditions there were very hazy and nitrate concentrations were observed to be particularly high on those days.

Background concentration samples were taken for one 24-h period, starting at 1300 PDT September 21, 1996, near Two Harbors on Santa Catalina Island, 35 km upwind of the mainland. Three cascade impactors (two MOUDIs with Teflon substrates and one MOI with aluminum foil substrates), a modified low-volume filter sampler, and a continuous UV photometric ozone monitor (Dasibi Environmental Corp., model 1003-AH) but no ATOFMS were used at this location.

The experiment was designed to permit a later search for "single air parcels" that pass consecutively over several air monitoring sites as they are transported across the basin. Previous experience with experiments designed to achieve this objective (6) suggested the following time schedule: intensive sampling was conducted in Long Beach at 0700–1100 PDT (Pacific Daylight Time), in Fullerton at 1100–1500 PDT, and in Riverside at 1500–1900 PDT. By combining the September 21–22 background measurements at Santa Catalina Island with the September 23–24 intensive experiments and the September 25–26 experiments at Riverside, a 6-day consecutive period of observations exists as air parcels are advected across the air basin. The relationship between instruments and sampling schedules is illustrated in Figure 2.

An electrical aerosol analyzer (EAA, TSI Inc., model 3030) was used at each site to measure particle number concentrations in the size range $0.017 < d_p < 0.250 \mu\text{m}$. The EAA at Fullerton was equipped with an electrometer having an improved amplifier for increased sensitivity. Each EAA was interfaced with a personal computer, which enabled the acquisition of a particle number distribution over this size range approximately once every 7 min.

Laser optical particle counters (OPC, Particle Measuring Systems, model ASAP-X) were used at two of the three sites (Long Beach and Riverside) to corroborate the size distribution data from the EAA over the size range where the two instruments overlap and to extend size distribution measurements to larger particle sizes. This instrument recorded particle number distributions in 31 channels over the size range $0.09 < d_p < 2.6 \mu\text{m}$ every 5 s. Size distributions from the OPC were corrected as suggested by Hering (47) to take

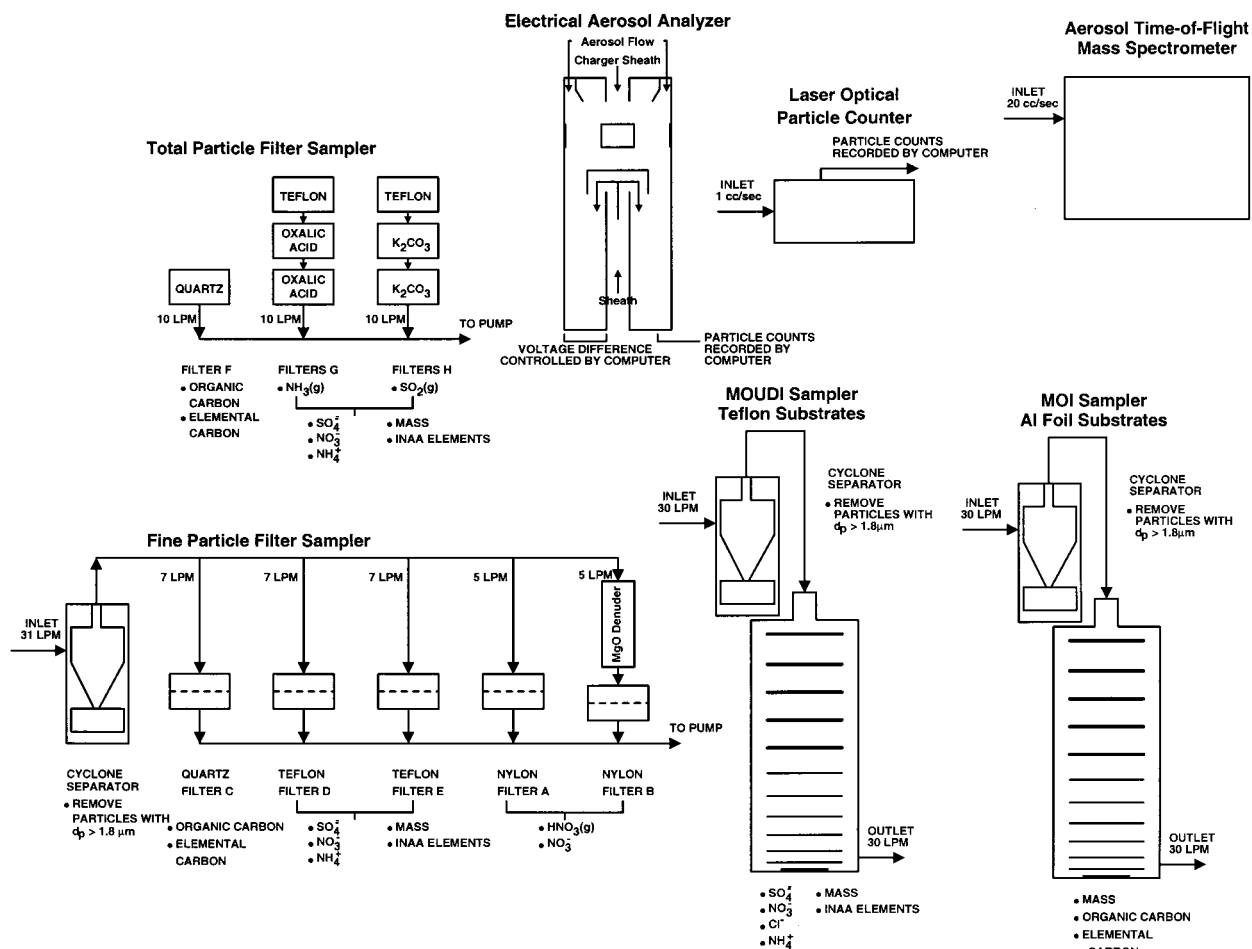


FIGURE 3. Schematic diagram of the particulate matter sampling systems used in this study.

into account the difference in the refractive index between the polystyrene latex (PSL) spheres used to calibrate the instrument and typical Los Angeles area atmospheric aerosols.

Three ATOFMS instruments were used; the Long Beach and Fullerton sites each had transportable ATOFMS systems (14), and a laboratory-bound ATOFMS (12) sampled in Riverside. Despite design differences between the transportable and laboratory-bound systems, the three ATOFMS instruments can be calibrated to yield essentially equivalent results through intercomparisons with the impactor and OPC data from this study (48). The ATOFMS instruments operated continuously, collecting number distribution data in the aerodynamic particle size range $0.2 < d_a < 5 \mu\text{m}$ and obtaining mass spectra for a subset of the input particle population.

Each air monitoring site was equipped with a pair of cascade impactors. One 10-stage rotating Micro-orifice Uniform Deposit Impactor (MOUDI, MSP Corp., model 100) (49) and one 10-stage nonrotating Microorifice Impactor (MOI, MSP Corp., model 110) (49) were operated simultaneously to measure fine particulate mass and chemical composition as a function of particle size. A Teflon-coated cyclone separator was placed upstream of each impactor in order to capture coarse particles ($d_a > 1.8 \mu\text{m}$) that might otherwise enter the impactor and distort the mass distribution measurements by bouncing from their appropriate collection stages. Particles reported here were collected on stages 5–10 of the impactors over the size range $0.056 < d_a < 1.8 \mu\text{m}$; the upper stages of the impactor also were loaded with impaction substrates but were not analyzed. The nonrotating impactor was loaded with aluminum foil substrates (MSP Corp.), while the rotating impactor was loaded with Teflon substrates

(Teflo, Gelman Science). No grease or oil was used on the substrates in order to avoid adding a source of organic contamination.

In addition to the above instruments, total (no size separation) and fine ($d_a < 1.8 \mu\text{m}$) airborne particle samples were collected using a low volume filter-based sampling system (see Figure 3). Total particulate matter was collected on one open-faced quartz fiber filter (Pallflex, 2500 QAO) and on two parallel open-faced Teflon filters (Gelman Sciences, Teflo, $2.0 \mu\text{m}$ pore size) at the flow rates shown in Figure 3. The two open-faced Teflon filters removed particles from the air, and the airstream then passed through several chemically impregnated backup filters designed for collection of certain reactive gases. A pair of oxalic acid-impregnated glass fiber filters (Gelman Type AE, 47 mm diameter), filters G in Figure 3, collected gas-phase ammonia to be detected as ammonium ion. A pair of K_2CO_3 -impregnated quartz fiber filters (Pallflex, 2500 QAO, 47 mm diameter), filters H in Figure 3, collected gas-phase SO_2 to be detected as sulfate ion. For fine particle samples, ambient air was passed through an acid-washed Pyrex glass inlet line to a Teflon-coated AIHL-design cyclone separator (50) at a nominal flow rate of 26 L min^{-1} before particle collection on a set of parallel filters: one quartz fiber filter (Pallflex, 2500 QAO, 47 mm diameter), two Teflon filters (Gelman Sciences, Teflo, $2.0 \mu\text{m}$ pore size, 47 mm diameter), and one prewashed nylon filter (Gelman Sciences, Nylasorb, 47 mm diameter). The flow rates sampled by these filters are shown in Figure 3. An additional nylon filter, located downstream of a MgO -coated diffusion denuder, was used in conjunction with the nylon filter downstream of the cyclone alone to measure gas-phase nitric acid and fine particle nitrate by the denuder difference

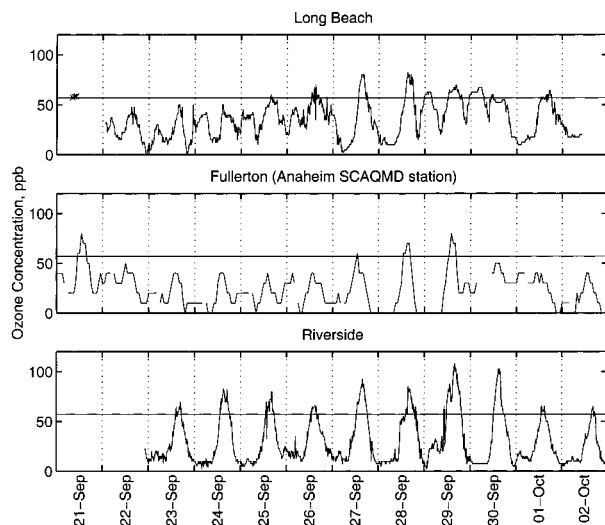


FIGURE 4. Ozone concentrations at all four sampling sites during the study. The solid horizontal line drawn at 57 ppb O_3 is supplied for reference purposes and indicates the average ozone concentration observed at the Santa Catalina Island background site based on measurements made on September 21–22, 1996. The “x” symbols on the Long Beach graph indicate the actual ozone concentrations measured at Santa Catalina Island, which did not vary greatly between daytime and nighttime samples.

method. The airflow rate through each filter or set of filters was measured before and after each 4-h sampling period with a calibrated rotameter. While these filter samples did not offer the size-specific information available from the impactor substrate samples, they served as an important check on the entire quantity of fine particle material in the atmosphere. These samples have the advantage of a greater available mass, thereby facilitating the chemical analysis procedures.

Mass concentration determinations were made from all foil and Teflon impactor substrates and Teflon filters and afterfilters by repeated weighing before and after sample collection on a Mettler model M-55-A mechanical microbalance maintained in a temperature- and humidity-controlled environment ($21.0 \pm 0.5^\circ\text{C}$, $37 \pm 3\%$ RH). Foil substrates were precleaned of any organic contaminants by baking for 40–50 h at 550°C , and all quartz fiber filters were precleaned by baking for at least 10 h at 550°C .

All impactor substrates and filters were cut in half before chemical analysis to allow the use of multiple chemical analysis methods. The samples collected on aluminum foil substrates and quartz fiber filters were analyzed for elemental and organic carbon using the thermal-optical carbon analysis method of Huntzicker et al. (51) as modified by Cary (52). One-half of each sample collected on a Teflon substrate underwent analysis by ion chromatography (Dionex Corp, model 2020i) for the anions NO_3^- , SO_4^{2-} , and Cl^- (53), and the extract also was analyzed by an indophenol colorimetric procedure for NH_4^+ (54) using an Alpkem rapid flow analyzer (model RFA-300). The second half of each Teflon impactor substrate was subjected to neutron activation analysis for trace elements detection (55). Gas-phase ammonia collected on oxalic acid-impregnated glass fiber filters was measured as ammonium ion using the indophenol colorimetric procedure cited above on the Alpkem rapid flow analyzer (model RFA-300). Gas-phase SO_2 collected on K_2CO_3 -impregnated quartz fiber filters was detected as sulfate ion by ion chromatography. Nylon filters upstream and downstream of an MgO -coated diffusion denuder permitted determination of gas-phase nitric acid and fine particle nitrate by the denuder difference method using the ion chromatographic

analysis procedures described by Solomon et al. (56). Detection limits for SO_4^{2-} , NO_3^- , NH_4^+ , and TC (total carbon) were 0.62, 0.53, 0.36, and $0.78 \mu\text{g}/\text{sample}$, corresponding to 0.17, 0.15, 0.10, and $0.43 \mu\text{g m}^{-3}$ for an impactor stage, for example.

Continuous gas-phase measurements were made for selected air pollutants at Long Beach and Riverside. O_3 (Dasibi Environmental Corp., model 1003-AH at Long Beach, model 1003-PC at Riverside) and NO/NO_2 (ThermoElectron Corp., model 14B/E) concentrations were measured at both Long Beach and Riverside. In addition, O_3 , NO , NO_2 , and CO data were obtained from nearby South Coast Air Quality Management District (SCAQMD) air monitoring stations.

Electropolished stainless steel canister samplers were used at Long Beach and Riverside to capture volatile organic compounds. The 6-L canisters were shipped and deployed into the field under high vacuum. The 4-h integrated samples were collected in the canisters through PFA Teflon sample lines purged with ambient air, after which the canisters were resealed. Total nonmethane organic compounds in the gas phase were measured by cryogenic preconcentration and direct flame ionization detection according to EPA Method TO12 (57). Individual organic compounds from the stainless steel canister samples were analyzed by gas chromatography/flame ionization detection.

Results and Discussion

Meteorology. To describe pollutant transport conditions over the September 21–October 3, 1996, sampling period, windfields were constructed according to the method of Goodin et al. (58). Meteorological data used as input to these calculations included hourly averaged wind speed and direction at 29 meteorological stations maintained by the South Coast Air Quality Management District.

Figure 1a,b illustrates the wind patterns characteristic of the period September 21–30, 1996. Figure 1a shows the calculated wind field in the study area at 0600 PDT on September 24, 1996. Wind speeds were very low. Overnight stagnation occurred across the air basin every night for 15–18 h, beginning at 1900–2200 PDT in the evening and ending at 1200–1500 PDT the following day. Figure 1b shows the calculated wind field on the afternoon of the same day at 1300 PDT. Stagnation had ended, and the wind was blowing onshore from the ocean in the general direction from southwest to northeast, providing the desired transport across the three urban air monitoring sites. The wind patterns changed during the second intensive period of operation, October 1–2, 1996. Figure 1c shows the calculated wind field in the area at 0600 PDT on October 1, 1996. Instead of the overnight stagnation seen the previous week, flow occurred up the coast from the southeast overnight. Figure 1d shows the calculated wind field on the same day at 1300 PDT. In the afternoon, the typical onshore sea breeze flow from the southwest toward the northeast was observed. The result of this set of wind patterns was that, during the October 1–2 period, air parcels travelled along a zigzag trajectory, first parallel to the coast, then inland, before being sampled at the air monitoring sites and did not pass over the three urban sites sequentially as had been hoped.

Weather conditions throughout the sampling period were mild and devoid of precipitation. No significant fog was reported onshore on days of intensive sampling. We did observe a fog bank offshore to the west of the Santa Monica Bay coastline during portions of the Santa Catalina Island background experiments (though not between that island and the mainland). Conditions at Long Beach in the morning during the intensive sampling periods were overcast with little to no breeze, temperatures ranging from 19 to 25°C , and humidity ranging from 45 to 75%. Fullerton during the late morning to early afternoon intensive sampling periods

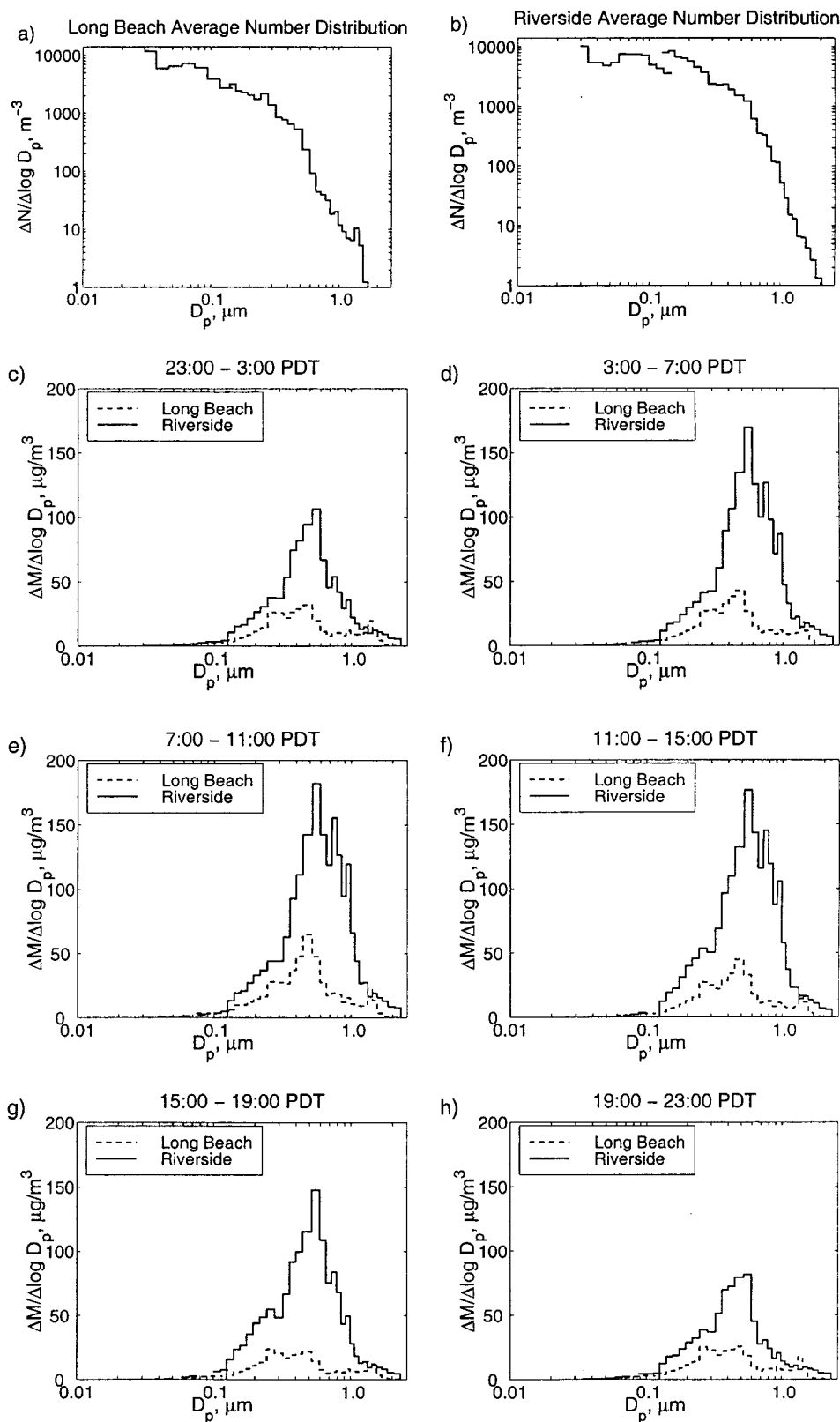


FIGURE 5. Particle number distributions measured by the EAAs and OPCs at (a) Long Beach and (b) Riverside, averaged over the course of the entire study. Particle mass distributions at Long Beach and Riverside averaged over the time intervals (c) 2300–0300 PDT, (d) 0300–0700 PDT, (e) 0700–1100 PDT, (f) 1100–1500 PDT, (g) 1500–1900 PDT, and (h) 1900–2300 PDT.

experienced patchy clouds with temperatures ranging from 19 to 27 °C and relative humidity ranging from 35 to 65%. Conditions at Riverside during the late afternoon intensive sampling periods included temperatures ranging from 17 to 32 °C and relative humidities ranging from 20 to 65%. At Riverside in the afternoon, skies were clear of clouds, but on

most days a haze due to photochemical smog was present. Maximum wind speeds were about 3 m s^{-1} .

Ozone. Continuous measurements of ozone concentrations were made alongside the sampling equipment at Santa Catalina Island, Long Beach, and Riverside. In addition, data on hourly average ozone concentrations at air monitoring

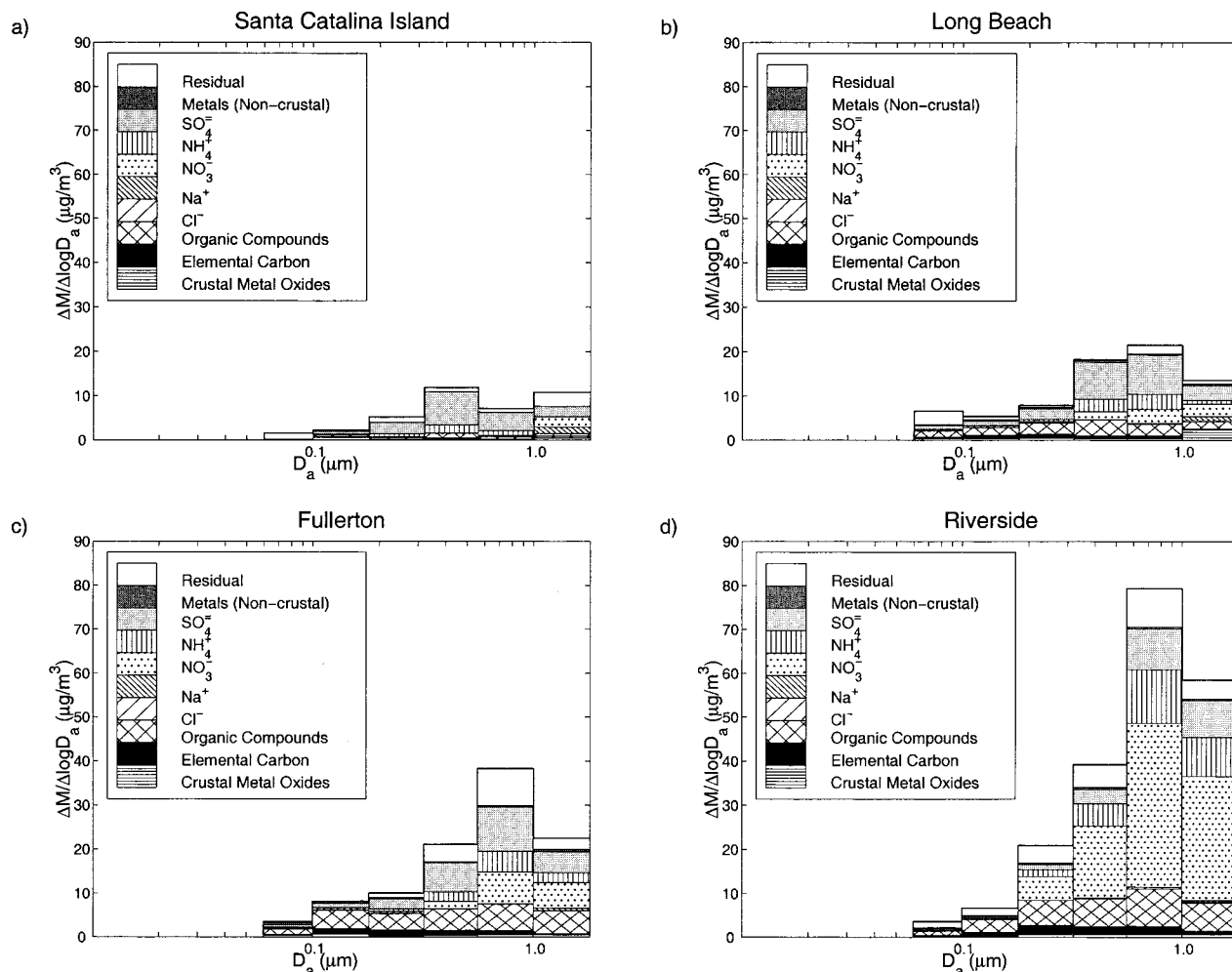


FIGURE 6. Size-dependent chemical composition of airborne particles in southern California averaged over all cascade impactor samples taken at each sampling site over the course of the study. Samples are taken at different times of the day at each site (see text).

stations near Fullerton and Riverside were made available by the SCAQMD. Results are shown in Figure 4. The ozone peak occurred at about 1500 PDT every day at all three urban locations. In addition, a secondary peak often occurred overnight at Long Beach, at 0100–0600 PDT. Ozone concentrations measured at the background site at Santa Catalina Island on September 21–22, 1996, were essentially constant both day and night at close to 57 ppb. It is interesting to note that the regional ozone background concentration, which averaged 57 ppb, is generally closer to the maximum inland concentrations than to the minimum inland concentrations during this period; the ozone depletion below the background levels seen overnight is likely due to O_3 scavenging by NO at night. With upwind regional background O_3 levels at 57 ppb, only modest O_3 increases above background are needed to reach the new U.S. national ambient air quality standard for ozone, which was set in 1997 at 0.08 ppm O_3 not to be exceeded over an 8-h averaging period on more than 4 days per year, averaged over 3 years (59).

Particle Size Distribution. Continuous particle size distribution measurements were made at Long Beach and Riverside throughout the study using OPCs. When these data are combined with data from the EAAs at those sites, continuous particle size distributions are obtained over the diameter range $0.017 < d_p < 3.0 \mu\text{m}$. Particle number distributions averaged over all hours of the study are shown in Figure 5a,b. These number distributions have been converted to mass distributions assuming a particle density of 1.3 g cm^{-3} and then averaged over all the study days in

4-h periods to demonstrate the diurnal differences in average particle mass distributions at Long Beach and Riverside (see Figure 5c–h). Throughout the study, the particle mass distribution at Riverside is largely unimodal in the submicron particle size range. The peak in the particle mass distribution at Riverside occurs at somewhat larger particle sizes ($0.5 \mu\text{m}$) than at Long Beach. This is in contrast to much of the data taken a decade earlier during the SCAQS experiments, which showed two modes in the particle mass distribution in the particle diameter range between $0.1 < d_p < 1.0 \mu\text{m}$, one at about $0.7 \mu\text{m}$ particle diameter, and another at about $0.2 \mu\text{m}$ particle diameter [see, for example, Eldering et al. (10)]. The mode at $0.2 \mu\text{m}$ diameter during the SCAQS experiments, which is absent at Riverside in the present experiment, was attributed to the primary particle emissions from diesel engines and other primary aerosol carbon sources (13). The relative reduction in the size of the $0.2 \mu\text{m}$ mode in the mass distribution in the present experiment suggests soot emission reductions over the past decade; more extensive sampling would be needed to confirm this hypothesis, but it agrees with the decreasing trend in fine elemental carbon concentrations observed in the Los Angeles area since 1982 (60), the dominant source of which is diesel engine exhaust (61).

Fine Particle Chemical Composition. The size distribution of the ambient aerosol chemical composition averaged over all cascade impactor data taken at the background site and at the three urban sites is shown in Figure 6. The background aerosol at Santa Catalina Island is almost entirely composed of inorganic substances. The urban sites show

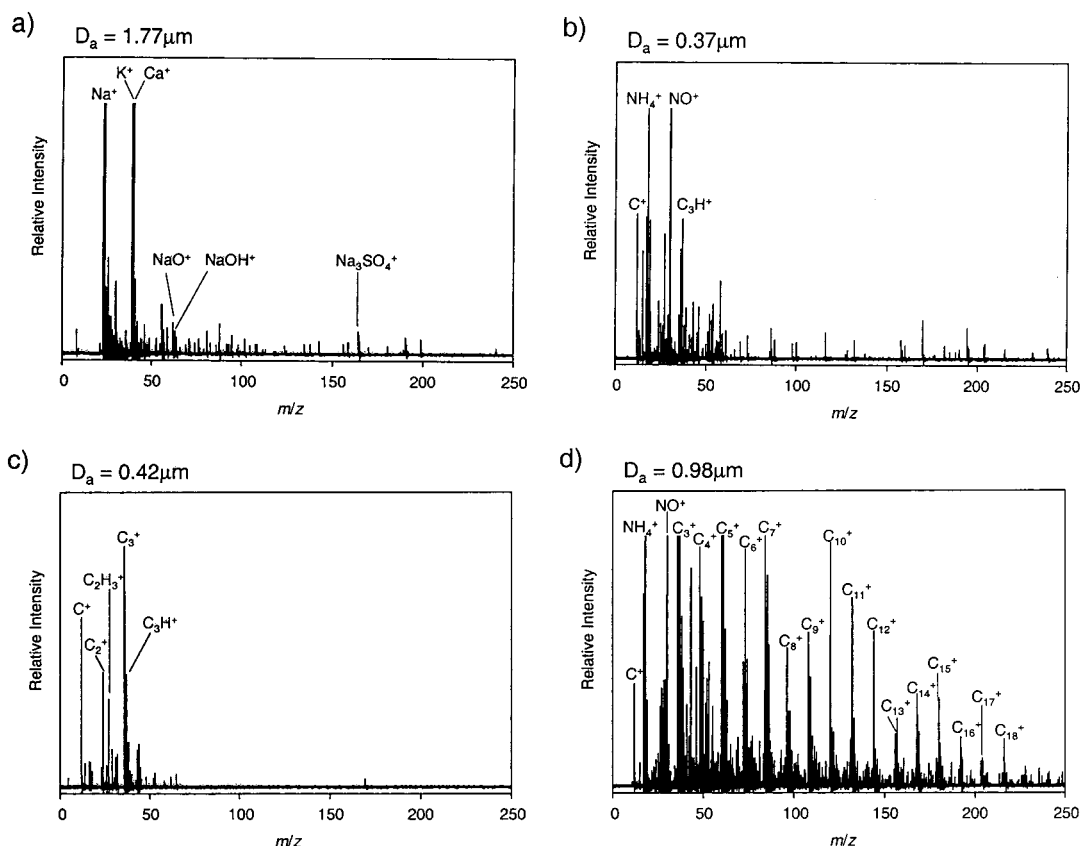


FIGURE 7. Mass spectra of particles sampled by ATOFMS during this study: (a) sea salt particle; (b) ammonium nitrate-containing particle with organic carbon inclusions; (c) organic carbon particle; (d) predominantly elemental carbon particle with some ammonium nitrate content.

additions of carbonaceous compounds to the background aerosol. The Riverside site is distinguished by large amounts of ammonium and nitrate in the aerosol, as has been seen previously (25, 62–64). Average fine sulfate concentrations measured at Long Beach and Riverside in the present study are lower than the September–October monthly average concentrations measured near these places in 1982, 1986, and 1993 (60).

Different numbers of impactor samples were taken at the different sites and on different days (see Figure 2). In future work, sets of these impactor samples taken on specific days as well as fine particle, total suspended particle, and gas-phase pollutant data, representing passage of the same air mass over successive sampling sites will be presented such that a Lagrangian rather than Eulerian view of particle evolution can be obtained (65).

Single Particle Chemical Composition. The aerosol time-of-flight mass spectrometers located at Long Beach, Fullerton, and Riverside are capable of drawing a continuous stream of particles from the atmosphere and determining both the size and chemical constituents of the individual particles present, one particle at a time. The particles are accelerated through a converging nozzle, after which three skimmers collimate the stream and diverging particles are pumped away. Remaining particles pass into the vacuum chamber of the instrument. As a particle passes through two laser beams consecutively, its velocity (which is dependent on particle aerodynamic diameter) is measured, and from that velocity the particle size is determined. Knowing the speed of the particle, a timing circuit is set to trigger a high-power desorption laser that intercepts the particle. The ions generated by laser desorption of species from the particle are swept into the mass spectrometer, where spectra indicating the elemental and molecular composition of the

particle are generated. The mass spectrometers sampled continuously throughout the periods shown in Figure 2. Depending on the instrument considered (transportable vs laboratory ATOFMS) mass spectra were acquired for 6–14% of the particles detected by the ATOFMS instruments, for a total of more than 319 000 individual particle spectra.

Examples of the mass spectra of characteristically different particles are shown in Figure 7. Figure 7a shows the positive ion mass spectrum of a sea salt particle of aerodynamic diameter 1.77 μm . The particle contains Na^+ , K^+ , and Ca^+ as the major positive ion constituents along with smaller amounts of Na_2SO_4^+ , indicative of sodium sulfate. In Figure 7b, the spectrum of an ammonium nitrate-containing particle of diameter 0.37 μm is shown. The key ions NH_4^+ and NO^+ that indicate ammonium and nitrate, respectively, are accompanied by C^+ and C_3H^+ , suggesting that this particle possibly is composed of a secondary ammonium nitrate coating over a primary carbon particle core in a way that qualitatively matches many of the particles predicted by the air quality model of Kleeman et al. (13). Figure 7c shows a 0.42 μm diameter particle that is composed of hydrocarbons and little else. Figure 7d depicts an elemental carbon-containing particle, indicated by fragments with integer numbers of carbon atoms, but little or no hydrogen. As in Figure 7b, the presence of ammonium nitrate indicator ions in the spectrum of this particle may represent a secondary ammonium nitrate coating.

The hundreds of thousands of individual particles that were characterized by the three ATOFMS instruments can be sorted into categories and used to display the time series of particles having specific chemical attributes. Examples of several such time series are presented in Figure 8. The threshold level for considering that a specific ion is present within a particle is that its peak area must constitute at least

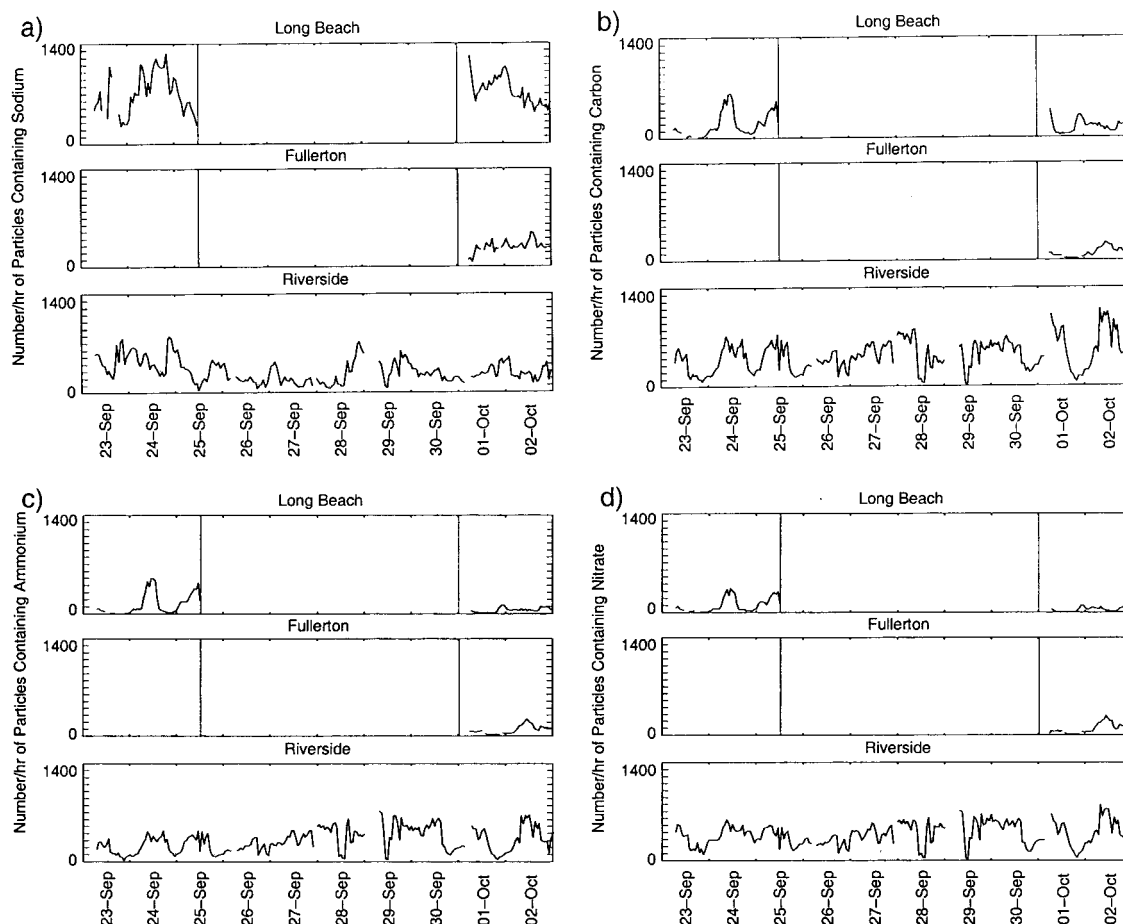


FIGURE 8. Time series showing relative number concentrations of (a) sodium-containing particles, a marker for sea salt; (b) carbon-containing particles; (c) ammonium-containing particles; and (d) nitrate-containing particles among those particles for which spectra were collected. These data have not been adjusted to reflect the counting efficiency of the ATOFMS instruments (48).

0.5% of the total peak area of the spectrum. Figure 8a shows the time series of sodium-containing particles. Sodium is one marker for sea salt-derived particles, though it is also found at times in smaller combustion particles. Not surprisingly, the sodium-containing particle concentrations are highest at the coastal Long Beach site. The number concentration of particles containing carbon is highest at Riverside, reflecting accumulation of the primary emissions from urban activities during air mass transit across the air basin, as seen in Figure 8b. The time series of particle counts for particles containing ammonium and nitrate are shown in Figure 8c,d. The time series appear to be nearly identical, and indeed the ammonium and nitrate are generally found within the same individual particles. Very close examination of the ammonium- and nitrate-containing particle counts shows that nitrate-containing particles exceed ammonium-containing particles at Riverside on some occasions, for example, during the times on September 23–25 when sodium-containing particle counts are elevated at Riverside. Examination of single particle spectra show sodium nitrate particles, reacted sea salt, to be present at Riverside at those times.

The ATOFMS systems offer time series data on the occurrence of particles containing specific chemical species with temporal resolution on the order of minutes (66). These instruments display particle counting characteristics that are more likely to detect particles at the larger end of the fine particle size range. The counting efficiency of the ATOFMS instruments as a function of particle size during this study has been determined by Allen et al. (48) through comparison with particle size distributions obtained from the cascade

impactors and optical particle counters. The method and results of that comparison are detailed in ref 48, which shows how to reconcile the data from the matched sets of conventional instruments and the two ATOFMS designs operated at the air monitoring sites. At present translation of relative peak heights or peak areas per spectrum for the various chemical species into absolute quantities of each chemical substance in a particle remains to be completed. Sensitivity factors that connect the relative abundance of some ions to their relative peak areas have been determined in the laboratory (67). The questions of particle counting efficiency and chemical sensitivity will be addressed further in future work both through additional laboratory experiments and through calibration of the ATOFMS systems according to the chemical composition data as a function of particle size collected by the cascade impactors during the present experiments.

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Literature Cited

- (1) Calvert, J. G.; Su, F.; Bottenheim, J. W.; Strausz, O. P. *Atmos. Environ.* **1978**, *12*, 197–226.
- (2) Pandis, S. N.; Harley, R. A.; Cass, G. R.; Seinfeld, J. H. *Atmos. Environ.* **1992**, *26A*, 2269–2282.
- (3) Stelson, A. W.; Friedlander, S. K.; Seinfeld, J. H. *Atmos. Environ.* **1979**, *13*, 369–371.
- (4) Stelson, A. W.; Seinfeld, J. H. *Atmos. Environ.* **1982**, *16*, 2507–2514.
- (5) Russell, A. G.; McRae, G. J.; Cass, G. R. *Atmos. Environ.* **1983**, *17*, 949–964.
- (6) Russell, A. G.; Cass, G. R. *Atmos. Environ.* **1986**, *20*, 2011–2025.
- (7) Gard, E. E.; Kleeman, M. J.; Gross, D. S.; Hughes, L. S.; Allen, J. O.; Morrical, B. D.; Fergenson, D. P.; Dienes, T.; Gaelli, M. E.; Johnson, R. J.; Cass, G. R.; Prather, K. A. *Science* **1998**, *279*, 1184–1187.
- (8) Larson, S. M.; Cass, G. R.; Gray, H. A. *Aerosol Sci. Technol.* **1989**, *10*, 118–130.
- (9) Zhang, X. Q.; McMurry, P. H.; Hering, S. V.; Casuccio, G. S. *Atmos. Environ.* **1993**, *27A*, 1593–1607.
- (10) Eldering, A.; Cass, G. R.; Moon, K. C. *Atmos. Environ.* **1994**, *28*, 2733–2749.
- (11) Phalen, R. F.; Cuddihy, R. G.; Fisher, G. L.; Moss, O. R.; Schlessinger, R. B.; Swift, D. L.; Yeh, H. C. *Radiat. Prot. Dosim.* **1991**, *38*, 179–184.
- (12) Noble, C. A.; Prather, K. A. *Environ. Sci. Technol.* **1996**, *30*, 2667–2680.
- (13) Kleeman, M. J.; Cass, G. R.; Eldering, A. J. *Geophys. Res.* **1997**, *102*, 21355–21372.
- (14) Gard, E. E.; Mayer, J. E.; Morrical, B. D.; Dienes, T.; Fergenson, D. P.; Prather, K. A. *Anal. Chem.* **1997**, *69*, 4083–4091.
- (15) Carson, P. G.; Neubauer, K. R.; Johnston, M. V.; Wexler, A. S. *J. Aerosol Sci.* **1995**, *26*, 535–545.
- (16) Murphy, D. M.; Thomson, D. S. *Aerosol Sci. Technol.* **1995**, *22*, 237–249.
- (17) Hinz, K. P.; Kaufmann, R.; Spengler, B. *Aerosol Sci. Technol.* **1996**, *24*, 233–242.
- (18) Hinz, K. P.; Kaufmann, R.; Spengler, B. *Anal. Chem.* **1994**, *66*, 2071–2076.
- (19) Reents, W. D.; Downey, S. W.; Emerson, A. B.; Muijsce, A. M.; Muller, A. J.; Siconolfi, D. J.; Sinclair, J. D.; Swanson, A. G. *Aerosol Sci. Technol.* **1995**, *23*, 263–270.
- (20) Kievit, O.; Weiss, M.; Verheijen, P. J. T.; Marijnissen, J. C. M.; Scarlett, B. *Chem. Eng. Commun.* **1996**, *151*, 79–100.
- (21) Prather, K. A.; Nordmeyer, T.; Salt, K. *Anal. Chem.* **1994**, *66*, 1403–1407.
- (22) Nordmeyer, T.; Prather, K. A. *Anal. Chem.* **1994**, *66*, 3540–3542.
- (23) Carson, P. G.; Johnston, M. V.; Wexler, A. S. *Aerosol Sci. Technol.* **1997**, *26*, 291–300.
- (24) Hidy, G. M.; Mueller, P. K.; Grosjean, D.; Appel, B. R.; Wesolowski, J. J., Eds.; *Advances in Environmental Science and Technology, Vol. 9: The Character and Origins of Smog Aerosols, A Digest of Results from the California Aerosol Characterization Experiment (ACHEX)*; John Wiley & Sons: New York, 1980.
- (25) Russell, A. G.; Cass, G. R. *Atmos. Environ.* **1984**, *18*, 1815–1827.
- (26) Russell, A. G.; McCue, K. F.; Cass, G. R. *Environ. Sci. Technol.* **1988**, *22*, 263–270.
- (27) Russell, A. G.; McCue, K. F.; Cass, G. R. *Environ. Sci. Technol.* **1988**, *22*, 1336–1347.
- (28) Hildemann, L. M.; Russell, A. G.; Cass, G. R. *Atmos. Environ.* **1984**, *18*, 1737–1750.
- (29) Lawson, D. R. *J. Air Waste Manage. Assoc.* **1990**, *40*, 156–165.
- (30) Wall, S. M.; John, W.; Ondo, J. L. *Atmos. Environ.* **1988**, *22*, 1649–1656.
- (31) McMurry, P. H. *Organic and elemental carbon size distribution of Los Angeles aerosol measurements during SCAQS: Final report to California Air Resources Board*; Technical Report A732-075; University of Minnesota: 1989.
- (32) McMurry, P. H.; Zhang, X. Q. *Aerosol Sci. Technol.* **1989**, *10*, 430–437.
- (33) Cahill, T. H.; Matsumura, R. F.; Surovick, M.; Unger, C.; Wilkenson, K. *Size-time-compositional analysis of aerosols during SCAQS: Final report to California Air Resources Board*; Technical Report A732-074; University of California—Davis: 1990.
- (34) Lurmann, F. W.; Wexler, A. S.; Pandis, S. N.; Musarra, S.; Kumar, N.; Seinfeld, J. H. *Atmos. Environ.* **1997**, *31*, 2695–2715.
- (35) Lu, R.; Turco, R. P.; Jacobson, M. Z. *J. Geophys. Res. A* **1997**, *102*, 6081–6098.
- (36) Jacobson, M. Z. *Atmos. Environ.* **1997**, *31*, 587–608.
- (37) Winkler, S. L.; Chock, D. P. *Environ. Sci. Technol.* **1996**, *30*, 1163–1175.
- (38) Cheng, M. D.; Gao, N.; Hopke, P. K. *J. Environ. Eng.* **1996**, *122*, 183–190.
- (39) Watson, J. G.; Chow, J. C.; Lu, Z. Q.; Fujita, E. M.; Lowenthal, D. M.; Lawson, D. R.; Ashbaugh, L. L. *Aerosol Sci. Technol.* **1994**, *21*, 1–36.
- (40) Gao, N.; Cheng, M. D.; Hopke, P. K. *Atmos. Environ.* **1994**, *28*, 1447–1470.
- (41) Pandis, S. N.; Wexler, A. S.; Seinfeld, J. H. *Atmos. Environ.* **1993**, *27*, 2403–2416.
- (42) Eldering, A.; Cass, G. R. *J. Geophys. Res. A* **1996**, *101*, 19343–19369.
- (43) Fraser, M. P.; Grosjean, D.; Grosjean, E.; Rasmussen, R. A.; Cass, G. R. *Environ. Sci. Technol.* **1996**, *30*, 1731–1743.
- (44) Grosjean, E.; Grosjean, D.; Fraser, M. P.; Cass, G. R. *Environ. Sci. Technol.* **1996**, *30*, 2704–2714.
- (45) Grosjean, E.; Grosjean, D.; Fraser, M. P.; Cass, G. R. *Environ. Sci. Technol.* **1996**, *30*, 2687–2703.
- (46) Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T.; Rasmussen, R. A. *Environ. Sci. Technol.* **1997**, *31*, 2356–2367.
- (47) Hering, S. V. *Aerosol Dynamics*, Inc., Berkeley, CA, personal communication, 1998.
- (48) Allen, J. O.; Hughes, L. S.; Kleeman, M. J.; Cass, G. R.; Gard, E. E.; Gross, D. S.; Galli, M. E.; Morrical, B. D.; Prather, K. A. *Environ. Sci. Technol.* Submitted for publication.
- (49) Marple, V. A.; Rubow, K. L.; Behm, S. M. *Aerosol Sci. Technol.* **1991**, *14*, 434–446.
- (50) John, W.; Reischl, G. J. *Air Pollut. Control Assoc.* **1980**, *30*, 872–876.
- (51) Huntzicker, J. J.; Johnson, R. L.; Shah, J. J.; Cary, R. A. In *Particulate Carbon, Atmospheric Life Cycle*; Wolff, G. T., Klimisch, R. L., Eds.; Plenum: New York, 1982; pp 79–88.
- (52) Birch, M. E.; Cary, R. A. *Aerosol Sci. Technol.* **1996**, *25*, 221–241.
- (53) Mulik, J.; Puckett, R.; Willims, D.; Sawicki, E. *Anal. Lett.* **1976**, *9*, 653–663.
- (54) Bolleter, W. T.; Bushman, C. T.; Tidwell, P. W. *Anal. Chem.* **1961**, *33*, 592–594.
- (55) Olmez, I. In *Methods of Air Sampling and Analysis*, 3rd ed.; Lodge, J., Ed.; Lewis Publishers: Chelsea, MI, 1989; pp 143–150.
- (56) Solomon, P. A.; Salmon, L. G.; Cass, G. R. *Environ. Sci. Technol.* **1992**, *26*, 1594–1601.
- (57) *Method for the determination of nonmethane organic compounds in ambient air using cryogenic preconcentration and direct flame ionization detection*; Technical Report EPA-600/4-89-018; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1988.
- (58) Goodin, W. R.; McRae, G. J.; Seinfeld, J. H. *J. Appl. Meteor.* **1979**, *18*, 761–771.
- (59) *Fed. Regist.* **40 CFR Part 50** **1997**, *62* (138), 38857.
- (60) Christoforou, C. S.; Salmon, L. G.; Hannigan, M. P.; Solomon, P. A.; Cass, G. R. *J. Air Waste Manage. Assoc.* In press.
- (61) Gray, H. A.; Cass, G. R. *Atmos. Environ.* **1998**, *32*, 3805–3825.
- (62) Gray, H. A.; Cass, G. R.; Huntzicker, J. J.; Heyerdahl, E. K.; Rau, J. A. *Environ. Sci. Technol.* **1986**, *20*, 580–589.
- (63) Solomon, P. A.; Fall, T.; Salmon, L.; Cass, G. R. *J. Air Pollut. Control Assoc.* **1989**, *39*, 154–163.
- (64) Chow, J. C.; Watson, J. G.; Fujita, E. M. *Atmos. Environ.* **1994**, *28*, 2061–2080.
- (65) Hughes, L. S.; Liu, D.-Y.; Allen, J. O.; Fergenson, D. P.; Kleeman, M. J.; Morrical, B. D.; Prather, K. A.; Cass, G. R. *Environ. Sci. Technol.* Submitted for publication.
- (66) Noble, C. A.; Prather, K. A. *Aerosol Sci. Technol.* **1998**, *29*, 294–306.
- (67) Gross, D. S.; Gaelli, M. E.; Silva, P. J.; Prather, K. A. *Anal. Chem.* Submitted for publication.

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